

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Manufacture of Urethanes

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improvements in or relating to the manufacture of polymeric materials, in particular to the manufacture of polyurethane materials from hydroxyl group-containing materials and organic isocyanates.

It is known to carry out the preparation of urethane group-containing materials by reacting hydroxylic compounds with isocyanates in the presence of catalysts. In particular it has been proposed to manufacture polyurethane products by the reaction of hydroxyl group-containing polymers with organic polyisocyanates using a variety of compounds as catalysts. Catalysts have proved valuable not only in accelerating the reactions, but in allowing lower operating temperatures and in affecting the relative rates of reaction of the isocyanate with for example hydroxyl group-containing materials and water. Catalysts that have hitherto been proposed suffer from certain disadvantages. Thus certain compounds of tin that have been proposed as catalysts, such as organotin compounds, promote oxidative degradation of polyurethanes based on for example polyethers. Salts of tin with organic acids, for example stannous octoate, that have been proposed as catalysts are unstable, and lose some of their activity when used in admixture with active hydrogen compounds.

It has now been found that the oxide,

hydrated oxide and hydroxide of divalent tin are valuable catalysts for the reaction of isocyanates with hydroxylic compounds the use of such compounds obviating or minimising the disadvantages associated with the use of the prior art catalysts.

Thus according to the present invention there is provided a process for the manufacture of urethane group-containing materials by the reaction of organic isocyanates with the hydroxyl group-containing compounds characterised in that the reaction is carried out in the presence of from 0.01% to 5% by weight of the hydroxyl group-containing compound of at least one compound selected from the oxide, hydrated oxide and hydroxide of divalent tin.

As organic isocyanate there may be used any organic mono or polyisocyanate. As hydroxyl group containing compound there may be used any organic mono or polyhydroxy compound.

The process of the present invention is particularly valuable for the manufacture of polyurethane products by the reaction of organic polyisocyanates with hydroxyl group-containing polymers containing at least two isocyanate-reactive groups per molecule.

Such polyurethane products may be rigid or flexible, cellular or homogeneous and may be prepared for example by methods and from materials fully described in the prior art, in the form of surface coatings, sheets, shaped articles or adhesive layers.

The hydroxyl group-containing polymer may be for example a polyester, polyesteramide or polyether or mixtures thereof. The polyesters or polyesteramides may be made for example from dicarboxylic acids, polyhydric alcohols and, as necessary, minor pro-

portions of diamines or aminoalcohols. Suitable dicarboxylic acids include succinic, glutaric, adipic, suberic, azelaic and sebacic acids as well as aromatic acids such as phthalic, isophthalic, and terephthalic acids. Mixtures of acids may be used. Examples of polyhydric alcohols include glycols such as ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, 2,3-butylene glycol, diethylene glycol tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, decamethylene glycol and 2,2-dimethyltrimethylene glycol. Other polyhydric alcohols containing more than two hydroxyl groups per molecule may be used, for example trimethylolpropane, trimethylethane, pentaerythritol and glycerol. Such compounds are included in varying amounts according to the desired rigidity of the products. Examples of diamines and aminoalcohols include ethylene diamine, hexamethylene diamine, monoethanolamine, phenylene diamines and benzidine.

As examples of polyethers for use in the process of the present invention there may be mentioned hydroxyl-ended polymers and copolymers of cyclic oxides, for example 1,2-alkylene oxides such as ethylene oxide, epichlorhydrin, 1,2-propylene oxide, 1,2-butylene oxide and 2,3-butylene oxide, oxacyclobutane and substituted oxacyclobutanes, and tetrahydrofuran. Such polyethers may be linear polyether glycols as are prepared, for example, by the polymerisation of an alkylene oxide in the presence of a basic catalyst, such as potassium hydroxide, and water or a glycol initiator. Alternatively there may be used branched polyethers prepared for example by the polymerisation of an alkylene oxide in the presence of a basic catalyst and a substance having more than two active hydrogen atoms per molecule, for example glycerol, hexanetriols, pentaerythritol and ethylene diamine. Mixtures of linear and branched polyethers may be used if desired.

Examples of suitable organic polyisocyanates include hexamethylene diisocyanate, tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3-methyldiphenylmethane-4,4'-diisocyanate, *m*- and *p*-phenylene diisocyanate, chlorophenylene-2,4-diisocyanate, naphthalene-1,5-diisocyanate, diphenyl-4,4'-diisocyanate, 4,4'-diisocyanato-3,3'-dimethyldiphenyl, diphenyl ether diisocyanate, 1,4-xylylene diisocyanate, 1,3-xylylene diisocyanate and dicyclohexylmethane-4,4'-diisocyanate. Triisocyanates which may be used include 2,4,6-triisocyanatotoluene and 2,4,4'-triisocyanatodiphenyl ether. Examples of other suitable organic polyisocyanates comprise the reaction products of an excess of a diisocyanate with polyhydric alcohols such as trimethylolpropane, and uretidione dimers and isocyanurate polymers of diisocyanates for example of tolylene-

2,4-diisocyanate. Mixtures of polyisocyanates may be used. Examples of suitable mixtures include the polyisocyanate compositions obtained by the phosgenation of the mixed polyamine reaction products of formaldehyde and aromatic amines such as aniline and orthotoluidine.

As described fully in the prior art the general methods of preparation of polyurethanes may include the incorporation in the polyurethane-forming mixture of various additives such as surface-active agents, for example oxyethylated phenols, oxyethylated fatty alcohols such as oleyl alcohol or sulphated dimethyl oleate, polyalkylsiloxanes, and copolymers thereof with polyalkylene oxides, flame-retardants such as  $\beta$ -trichloroethyl phosphate, and antimony oxide, plasticisers such as tricresyl phosphate and dioctyl phthalate, antioxidants and colouring matters and fillers such as carbon black and silica. Other types of catalyst, for example soluble organic compounds of metals, for example of the transition metals, such as iron and manganese acetylacetonate, and of tin and antimony, for example dibutyltin dilaurate and stannous octoate, may also be incorporated. A further class of additive that may be added comprises antioxidants, for example tert-butylcatechol and sterically hindered phenols.

The tin catalysts of the process of the present invention may be incorporated in the reaction mixture of organic isocyanate and hydroxyl group-containing compound in any convenient manner. As the tin compounds as hereinbefore defined are substantially insoluble in the reactants it is preferred that they should be added in the form of a dispersion.

Such a dispersion may be formed in any suitable dispersion medium for example there may be used a dispersion of the tin compound in one of the reactants such as the hydroxyl group-containing compound or alternatively a dispersion of the tin compound may be formed in one of the various additives which, as is described fully in the prior art, may be incorporated in the polyurethane forming mixture.

Examples of hydroxyl group-containing compounds which are suitable as dispersing media include polyethers, polyesters and polyesteramides as previously defined.

Examples of additives used in the manufacture of polyurethanes and which are suitable as dispersing media include surface active agents such as reaction products of alkylene oxides and phenols, polyalkyl siloxanes and copolymers thereof with alkylene oxides, flame retardants such as  $\beta$ -trichloroethyl phosphate and plasticisers such as tricresyl phosphate, dioctylphthalate. The dispersing medium may also consist of a mixture of such compounds.

The dispersion of the tin compound may be carried out in any convenient manner for example the tin compound may be dispersed in the dispersion medium by stirring the two components together with a high speed stirrer, optionally in the presence of a dispersing agent.

A dispersing agent is especially desirable when the dispersion medium is the hydroxyl group-containing compound.

As examples of suitable dispersing agents there may be mentioned anionic, cationic and neutral dispersing agents such as sodium or ammonium salts of long chain fatty acids, sulphated and sulphonated aliphatic and aromatic compounds, fully substituted quaternary ammonium salts containing long aliphatic chains, and condensation products of alkylphenols and alkylene oxides.

The proportion of tin compound incorporated in the process of the present invention may be between 0.01% and 5% and preferably between 0.05% and 1% of the weight of the hydroxyl group containing material.

The tin compounds used in the process of the present invention may be prepared by any of the methods described in the prior art, for example stannous oxide may be prepared by dehydration of the precipitate of hydrated stannous oxide obtained when stannous salts are treated with alkalis. Stannous hydroxide has not been isolated as a definite compound but it is present in a hydrated form in the precipitate obtained by adding alkalis or ammonia or alkali metal or ammonium salts of weak acids to an aqueous solution of a stannous compound. The form of the product may be modified by carrying out the precipitation in the presence of dispersing agents and/or other metallic salts. The rate of precipitation of the stannous compound may be altered and in particular, decreased by having present complexing agents, for example tartrates and citrates, which are known from the prior art to suppress precipitation of metal hydroxides. The precipitates and colloidal solutions of stannous compounds may be used for the purposes of the present invention. The almost clear solutions initially obtained by neutralising solution of stannous salts in the presence of complexing agents also may be used.

A preferred catalyst for the process of the present invention is the hydrated oxide of divalent tin obtained by the addition of an alkali hydroxide or ammonia to a stannous salt.

It has been found particularly advantageous in the process of the present invention to generate the preferred catalyst *in situ* in a suitable dispersion medium thus obtaining the catalyst in a finely divided and dispersed form ready for incorporation in the urethane-forming mixture.

Thus in a preferred embodiment of the

present invention there is provided a process for the manufacture of urethane group-containing materials by the reaction of an organic polyisocyanate with a hydroxyl group-containing polymer containing at least two isocyanate-reactive groups per molecule, characterised in that the reaction is carried out in the presence of the precipitate obtained by the addition of an alkali hydroxide or ammonium hydroxide to a stannous salt, said precipitate being formed *in situ* in the hydroxyl group-containing polymer or in an additive known to be used in the manufacture of polyurethane products.

Hydroxyl group-containing polymers containing at least two isocyanate-reactive groups per molecule suitable for use in the preferred embodiment of the present invention include polyethers and polyesters as hereinbefore described.

Additives such as are known to be used in the manufacture of polyurethane products, which are suitable for use in the *in situ* preparation of the catalyst of the preferred embodiment of the present invention include condensation products of phenols and alkylene oxides, polyalkylsiloxanes and copolymers thereof with alkylene oxides, flame retardants such as  $\beta$ -trichloroethyl phosphate, plasticisers such as tricresyl phosphate, dioctyl phthalate and organic carboxylic acids, for example stearic and oleic acids.

The above described precipitate may be prepared *in situ* in the preferred embodiment of the present invention in any convenient manner, for example a stannous salt such as stannous chloride dihydrate may be suspended in the molten or solid state in for example a polyether and the calculated quantity of an alkali hydroxide, such as sodium hydroxide, added whilst stirring the mixture at high speed. The hydrated stannous hydroxide thus formed is in the form of a finely dispersed colloidal precipitate.

It has been found that the process of the present invention is especially advantageous when applied to the manufacture of foamed, cellular polyurethane products by the reaction of hydroxyl group-containing polymers such as polyesters, polyesteramides and polyethers containing at least two isocyanate-reactive groups per molecule with organic polyisocyanates in the presence of water and/or a low boiling point liquid.

Suitable low boiling point liquids are liquids that are chemically inert towards isocyanates and water and have boiling points not exceeding 75°C, preferably between 15 and 50°C, for example fluorinated alkanes such as monofluorotrichloromethane, dibromodifluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane.

Such liquids are usually employed in amounts of from 10 to 100%, preferably from

25 to 60%, by weight of the hydroxylic polymer.

Water is usually employed in amounts of from 1 to 10% by weight of the hydroxyl group-containing polymer, when this is used as the source of carbon dioxide blowing gas.

Water may also be conveniently used in the dispersion of the tin catalysts of the process of this invention. For example, an aqueous solution of an alkaline hydroxide may be added to a mixture of a divalent tin salt such as stannous chloride, and the dispersing medium for example, a condensation product of a phenol and ethylene oxide.

The use of the tin catalysts of the process of the present invention in the preparation of foamed polyurethanes leads to the formation of products with superior mechanical properties, for example, hardness, (compression modulus) and tear strength. The foamed products also possess enhanced thermal stability and show marked resistance to oxidative degradation on heating.

The preparation of the foamed, cellular polyurethanes may be carried out by the general methods fully described in the prior art. Thus the materials may be mixed continuously or discontinuously and the hydroxyl group-containing polymer may be first reacted with part or the whole of the organic polyisocyanate before the final reaction to give a foam is carried out in a second stage. However it is generally preferred to carry out the foam preparation in one stage only, by the simultaneous reaction of the foam-forming ingredients, namely the hydroxyl group-containing polymer, the organic polyisocyanate and the water and/or the low boiling point liquid. This convenient one-stage process cannot be satisfactorily carried out with all hydroxyl group-containing polymers. In particular those polymers containing predominantly secondary hydroxyl end-groups do not normally give satisfactory foams using a one-stage process as defined above: using such polymers the foam-forming mass usually partially or wholly collapses with considerable loss of gas and the formation of unsatisfactory high density products. The one stage process gives particularly unsatisfactory results using polyethers having predominantly secondary hydroxyl end groups.

It has now been found that highly attractive low density foamed products may be obtained by a one-stage process by incorporating a tin compound of the type already referred to above.

Thus according to a further preferred embodiment of the present invention there is provided a process for the manufacture of foamed, cellular polyurethane products by the simultaneous interaction of a secondary hydroxyl-ended polymer, especially a polyether, an organic polyisocyanate and water and/or a low boiling point liquid, charac-

terised in that there is present the oxide, hydrated oxide or hydroxide of divalent tin.

Examples of predominantly secondary hydroxyl-ended polymers include polyesters and polyesteramides prepared from an excess of polyhydric alcohol and amine compound over dicarboxylic acid, wherein the polyhydric alcohol contains secondary hydroxyl groups, for example propylene glycol, 1,3-butylene glycol or glycerol. Secondary hydroxyl-ended polyethers include polymers and copolymers of 1,2-alkylene oxides such as propylene and butylene oxides. It is preferred to use predominantly secondary hydroxyl-ended polymers of propylene oxide, especially those with molecular weights of from 400 to 6000.

The advantageous results of the use of the tin catalysts used in the process of the present invention are enhanced by using in addition of said tin catalysts, basic catalysts comprising tertiary amines such as are described in the prior art as catalysts for the reaction of isocyanates with hydroxyl compounds, in particular for polyurethane formation. Such tertiary amine catalysts may be for example basic compounds containing at least one nitrogen atom attached directly to two or three organic radicals, for example hydrocarbon radicals which may contain one or more hetero atoms. The radicals may be for example, aromatic radicals such as phenyl or heterocyclic radicals such as pyridine, but it is preferred that at least two and preferably all the radicals should be aliphatic, cycloaliphatic or arylaliphatic radicals, which may form a ring with the nitrogen atom of the tertiary amine; for example a piperidine ring formed with a pentamethylene radical. The nitrogen atom may also be a member of more than one ring, for example as in triethylenediamine.

Examples of suitable tertiary amine catalysts include tetramethylguanidine, trimethylamine, triethylamine, tri(n-butyl)amine, dimethylethylamine, dimethylcyclohexylamine, dimethyl- and diethyl-benzylamine, N-methyl- and N-ethyl-morpholine, N-butyl-morpholine, N-methyl-, N-ethyl- and N-propyl-piperidine, N,N',N''-pentamethyldiethylenetriamine, N-methylpyrrolidine, 1,4-diazabicyclo[2,2,2]octane, pyrrolizidine, 8-methylpyrrolizidine, quinuclidine, N,N'-tetramethylethylenediamine, N,N'-tetramethylhexamethylenediamine, pentamethylguanidine, tetramethyl-1,3-butandiamine, 2-diethylaminoethyl phenyl ether, 2-diethylaminoethyl benzyl ether, 1,4-bis(pyrrolidino)-n-butane, N,N'-dimethylpiperazine,  $\beta$ -diethylaminopropionamide, 2-diethylaminoethyl acetate, 2-diethylaminoethylcarbanilate, di(2-diethylaminoethyl) adipate and fully N-substituted 4-aminopyridines in particular 4-dimethylaminopyridine and 4-pyrrolidinylpyridine. More than one tertiary amine may be used simultaneously. It should be understood that the above list of tertiary

amines is merely a list of compounds representing various classes of tertiary amine suitable for use in the process of the present invention.

- 5 Particularly preferred tertiary amines are 4-dimethylaminopyridine, 4-pyrrolidinylpyridine and 1,4-diazabicyclo(2,2,2)-octane.

- 10 The tertiary amine catalyst is usually incorporated in amounts of from 0.025% to 2.5% and preferably of from 0.1% to 1.0% based on the weight of the hydroxyl group-containing compound.

- 15 The improvements obtained by the use of the tin catalysts of the present invention in conjunction with tertiary amines are particularly valuable in the one-stage process for making polyurethane foams by the simultaneous interaction of a predominantly hydroxyl-ended polyether, an organic polyisocyanate and water.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight except where otherwise stated.

25 **EXAMPLE 1**

- 113 Parts of stannous chloride dihydrate were stirred at 40–50°C with 500 parts of the condensation product of 1 mole of nonylphenol with eight moles of ethylene oxide until a clear mixture was obtained. The mixture was then vigorously stirred at room temperature and a solution of 40 parts of sodium hydroxide in 272 parts of water was added dropwise over 2½ hours. After stirring for a further ½ hour, a thick non-basic paste was obtained.

- 37 Parts of the paste were mixed with 400 parts of a polyether prepared by condensation of glycerol and propylene oxide and having an approximate molecular weight of 3000 and hydroxyl value of 56 mgKOH/g, which has been previously warmed to 40°C. 3.2 Parts of an alkylsilane polyoxyalkylene block copolymer were added with stirring followed by 152 parts of an 80:20 mixture of tolylene-2,4- and tolylene-2,6-diisocyanates. The mixture was stirred, and at the commencement of foaming, was poured into a mould when a white low density flexible foam possessing a fine internal structure was rapidly obtained.

- The same procedure was repeated 5 days later using the same sample of paste as prepared above. A low density flexible foam similar to the one obtained above was obtained.

**EXAMPLE 2**

- 11.3 Parts of stannous chloride dihydrate were heated to 40–50°C with 50 parts of the polyether condensate used in Example 1, with stirring until a homogeneous mixture was obtained. After cooling to room temperature the mixture was rapidly stirred, and a solution of 4 parts of sodium hydroxide in

27.2 parts of water was added slowly. A thick, almost black neutral paste was obtained.

380 Parts of the polyether of Example 1 were warmed to 40°C, and mixed with 37 parts of the paste obtained above. 3.2 Parts of an alkylsilane polyoxyalkylene block copolymer were added, followed by 152 parts of an 80:20 mixture of tolylene-2,4- and tolylene-2,6-diisocyanates. After vigorous stirring, the mixture commenced to foam, and was poured into a mould when a grey-brown low density flexible foam was obtained.

**WHAT WE CLAIM IS:—**

1. Process for the manufacture of urethane group-containing materials by the reaction of organic isocyanates with hydroxyl group-containing compounds characterised in that the reaction is carried out in the presence of from 0.01% to 5% by weight of the hydroxyl group containing compound of at least one compound selected from the oxide, hydrated oxide and hydroxide of divalent tin.

2. Process for the manufacture of urethane group-containing materials as claimed in Claim 1 wherein the organic isocyanate is an organic polyisocyanate, the hydroxyl group-containing compound is a hydroxyl group-containing polymer containing at least two isocyanate-reactive groups per molecule, whereby there is obtained a polyurethane product.

3. Process for the manufacture of urethane group-containing materials as claimed in either of Claims 1 or 2 wherein the oxide, hydrated, oxide or hydroxide of tin is present in the form of a dispersion.

4. Process for the manufacture of urethane group-containing materials as claimed in any of the preceding claims wherein the oxide, hydrated oxide or hydroxide is incorporated in an amount of from 0.05% to 1% by weight of the weight of the hydroxyl group-containing material.

5. Process for the manufacture of urethane group-containing materials as claimed in any of the preceding claims wherein the hydrated oxide of tin is obtained by the addition of an alkali hydroxide or ammonia to a stannous salt.

6. Process for the manufacture of urethane group-containing materials as claimed in Claim 5 wherein the hydrated oxide of tin is in the form of a precipitate obtained by the addition of an alkali hydroxide or ammonia to a stannous salt, said precipitate being formed in situ in the hydroxyl group-containing polymer or in an additive known to be used in the manufacture of polyurethane products.

7. Process for the manufacture of urethane group-containing materials as claimed in Claim 2 wherein the hydroxyl group-containing polymer and organic polyisocyanate are

reacted in the presence of water and/or a low boiling liquid, whereby the polyurethane product obtained is a foamed, cellular polyurethane product.

5. 8. Process for the manufacture of urethane group-containing materials as claimed in Claim 7 wherein the hydroxyl group-containing polymer is a secondary hydroxyl-ended polymer and the said polymer, organic polyisocyanate and water are interacted simultaneously.

- 10 9. Process for the manufacture of urethane group-containing materials as claimed in Claim 8 wherein the secondary hydroxyl-ended polymer is a polyether.

- 15 10. Process for the manufacture of urethane group-containing materials as claimed in Claim 9 wherein the polyether is a secondary hydroxyl-ended polymer of propylene oxide having a molecular weight of from 400 to 6000.

- 20 11. Process for the manufacture of urethane group-containing materials as claimed in any of the preceding claims wherein the reaction

is carried out in the presence of a tertiary amine. 25

12. Process for the manufacture of urethane group-containing materials as claimed in Claim 11 wherein the tertiary amine is 4-dimethylaminopyridine, 4-pyrrolidinylpyridine or 1,4-diazabicyclo(2,2,2)octane. 30

13. Process for the manufacture of urethane group-containing materials as claimed in either of Claims 11 or 12 wherein the tertiary amine is used in an amount of from 0.025% to 2.5% and preferably from 0.1% to 1.0% by weight based on the weight of the hydroxyl group-containing polymer. 30

14. Process for the manufacture of urethane group-containing materials as claimed in Claim 1 and as hereinbefore described especially with reference to the Examples. 35

15. Urethane group-containing materials whenever manufactured by a process claimed in any of the preceding claims. 40

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